EUROPEAN PATENT SPECIFICATION

(12)

(54) **A reflection type mask**

Reflexionsmaske

Masque par réflection

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(56) References cited:
    EP-A- 55 077   EP-A- 252 734
    WO-A-87/06028

    • PATENT ABSTRACTS OF JAPAN, vol. 10, no. 19
      (P-423)[2076], 24th January 1986; & JP-A-60 173
      551 (HIDEKI MATSUMARA) 06-09-1985
    • APPLIED PHYSICS LETTERS, vol. 45, no. 1, 1st
      July 1984, pages 3-5, American Institute of
      Pgysics, New York, US; H. MATSUMURA et al.:
      "Demagnified projection printing by a new x-ray
      lithographic technique using no thin-film
      masks"
    • APPLIED OPTICS, vol. 23, no. 11, 1st June 1984,
      pages 1794-1801, Optical Society of America,
      New York, US; B. VIDAL et al.: "Metallic
      multilayers for x rays using classical thin-film
      theory"
    • APPLIED PHYSICS LETTERS, vol. 20, no. 9, 1st
      May 1972, pages 365-367, New York, US; E.
      SPILLER: "Low-loss reflection coatings using
      absorbing materials"

EP 0 279 670 B1

Description

This invention relates to a reflection type mask usable in the manufacture of semiconductor devices such as integrated circuits, large scale integrated circuits, etc. More particularly, the invention is concerned with a reflection type mask suitably usable with an exposure apparatus that uses, for exposure of workpieces such as wafers, a radiation energy such as X-rays of a wavelength in the range of 0.5-30 nm (5 - 300 Å) or vacuum ultraviolet radiation of a wavelength in the range of 30-200 nm (300 - 2000 Å) (hereinafter, these rays will be referred to as "soft X-rays"). This invention also relates to an exposure method and to an apparatus each using a reflection type mask.

It has been considered to use a reflection type mask with a projection exposure of the type using soft X-rays to print a pattern on a wafer. It may be considered to manufacture such a reflection type mask, particularly a reflective portion thereof, in the following two ways:

One is to use a natural crystal (single crystal) to provide a reflecting surface. The other is to grind the surface of a substrate to provide a total reflection mirror.

The former (see for example European patent application EP 0 055 077) utilises Bragg diffraction of the natural (single) crystal. Thus, when a radiation of a wavelength of 10 nm (100 Å) is used, it is necessary to use such a natural crystal having a grating constant not less than 5 nm (50 Å), according to the Bragg diffraction theory $2d \sin\theta = \lambda$ where d is the thickness, λ is the wavelength and θ is the angle defined between the incident ray and the substrate. It is very difficult to obtain such a crystal. If, on the other hand an ordinarily available natural crystal as having a grating constant in the range of 0.15-0.5 nm (1.5 - 5 Å) is used, the wavelength must be in an order of 0.5 nm (5 Å). However, at present, there is no resist material that has a sufficient sensitivity to such very short wavelength range.

The latter utilises the theory of total reflection by a mirror surface. However, because of the limitation to the material usable, the limitation to the ambient conditions and so on, a large critical angle such as of an order of 86 - 87 degrees has to be used. This means that the X-rays should be incident at near grazing incidence to the surface. This is generally inconvenient for pattern projection.

The present invention has been made having regard to the aforesaid problems and disadvantages, and provides a solution.

In accordance with the present invention there is provided a reflection type mask usable in an exposure apparatus having a projection optical system with a plurality of mirrors provided between the mask and a workpiece, for transferring a pattern of the mask onto the workpiece with soft X-ray or vacuum ultraviolet radiation, characterized in that:

said mask has a reflective surface provided by a multilayered film, and a non-reflective portion provided in or upon said reflective surface to define the pattern, and wherein said non-reflective portion is effective to attenuate the soft X-ray or vacuum ultraviolet radiation.

It is an advantage of the reflection type mask aforesaid that it can be manufactured easily and economically.

It is a further advantage that such reflection type mask can assure high resolution and contrast in the transfer of a pattern onto a workpiece.

Other features and advantages of the present invention will become apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

In the accompanying drawings:

Figure 1 is a schematic view of an optical path of a projection optical system suitable for use with a reflection type mask embodying the present invention;

Figure 2 is a schematic section showing the structure of a reflection type mask according to a first embodiment of the present invention;

Figures 3A-3C are schematic sections, respectively, for explaining the process of manufacture of the mask of the first embodiment;

Figure 4 is a schematic section showing the structure of a reflection type mask according to a second embodiment of the present invention;

Figure 5 is a schematic section for explaining a problem of half shade;

Figures 6A - 6C are schematic sections, respectively, for explaining the process of manufacture of the mask of the second embodiment; and

Figure 7 is a schematic section showing the structure of a reflection type mask according to a third embodiment of the present invention.

To assist in a better understanding of this invention, a detailed description of preferred embodiments will be given now. The description which follows is intended to be by way of example only.

In the embodiments described below a reflection surface of a mask is provided by a reflective portion having a multilayered structure.

Fresnel reflection theory is used to improve the reflection efficiency at the interfaces of the layers and, additionally, the Bragg diffraction theory is used so that the reflected lights from the interfaces of the layers interfere with each other to mutually the intensity. The thickness of each layer is determined so as to satisfy these conditions.

Details of the theory of reflection in a multilayered structure are fully discussed in "Low-Loss Reflection Coatings Using Absorbing Materials" by Eberhard Spiller ("Appl. Phys. Lett." Vol. 20, No. 9, May 1972) and "Metallic Multilayers for X-rays Using Classical Thin-Film Theory" by B. Vidal and P. Vincent ("Applied Optics" Vol.

23, No. 11/1, June 1984).

In the multilayered structure of the present invention, the materials of the layers and the thicknesses of the layers are selected and determined so as to meet both of the Bragg diffraction and the Fresnel reflection conditions:

$$nd \cos\theta = \lambda \, N/2 \qquad (1)$$

wherein d is a grating constant (film thickness), θ is the angle of incidence, λ is the wavelength, N is an integral number and n is the refractive index; and

$$\left| (N_1 - N_2) \right| / \left| (N_1 + N_2) \right|^2 = R \qquad (2)$$

wherein R is the Fresnel reflection factor, N_1 and N_2 are refractive indices of the materials of the multilayered film, each of which can be expressed by "N = n+ik" (where n represents the real number portion while ik repreents the imaginary number portion) in respect to the wavelength region of X-rays or ultraviolet rays.

Figure 1 shows a projection optical system of an X-ray exposure apparatus which may be used with a reflection type mask of the present invention so as to print, by projection exposure, a pattern of the mask upon a semiconductor wafer at a reduced scale. As illustrated, the projection system includes three mirrors M1, M2 and M3 each being adapted to reflect soft X-rays in this example. The first and third mirrors M1 and M3 have concave mirror surfaces, respectively, while the second mirror M2 has a convex mirror surface. Details of such a projection optical system usable in an X-ray exposure apparatus are disclosed in European Patent Application EP 0252734.

Figure 2 shows a reflection type mask according to a first embodiment of the present invention. The mask of this embodiment is suitable for use with a radiation of wavelength 12.4 nm (124 Å) as the exposing radiation.

The mask includes a substrate 1 which may be formed by a silicon single crystal plate having a ground surface having surface roughness not larger than 1.0 nm (10 Å)(rms). On the surface of the substrate 1, a large number of layers is formed, although only some of which are shown in the drawing for ease in illustration. In this embodiment, two different materials are used for these layers, in an alternating fashion. More specifically, first type layers 2, 4 ... are made of ruthenium (Ru) having a refractive index N = 0.91 + 6.8 x 10^{-3}i. Second type layers 3, 5 ... are made of silicon carbide (SiC) having a refractive index N = 1.02 + 3.7 x 10^{-3}i. The first type layers and the second type layers are formed alternately, as illustrated, to provide a reflective base portion 10 of multilayered structure.

In a particular example, the first type layers and the second type layers were made by sputtering deposition after a super high vacuum pressure not greater than

1x10^{-6} Pa was achieved and with an argon pressure of 5x10^{-1} Pa. Each of the first type layers had a thickness of 2.98 nm (29.8 Å) while each of the second type layers had a thickness of 3.39 nm (33.9 Å). Forty-one layers comprising the first type layers of a number twenty-one and the second type layers of a number twenty were formed on the substrate. Additionally, a surface layer of carbon (C) was formed with a thickness 1.0 nm (10Å) upon the top layer as a protection film B (Figure 3A), whereby a reflective base portion of multilayered structure was obtained. It is preferable that the first type layers have a refractive index whose real number portion is smaller while the second type layers have a refractive index whose real number portion is larger. This is because, as will be readily understood from the Fresnel reflection theory, such a material whose refractive index has a large difference from that of an ambience, such as an air, should preferably be used as the material of the final layer.

The thickness of each layer can be determined in accordance with the aforementioned Bragg diffraction formula and on the basis of the refractive index of each material and the wavelength of the radiation to be used. In the present embodiment, for example, the thickness can be determined as follows:

From the aforementioned Bragg diffraction formula (1), it follows that:

$$2(n_1 d_1 + n_2 d_2)\cos\theta = (2m)\lambda/2 \qquad (3)$$

wherein n_1 and n_2 are refractive indices of the materials used, d_1 and d_2 are the thickness of the layers of different materials, λ is the wavelength of radiation to be used, and m is an integral number. Where the angle of incidence is zero (i.e. the regular or perpendicular incidence), then cos $\theta=1$. Therefore, equation (3) can be rewritten as follows:

$$n_1 d_1 + n_2 d_2 = \lambda(m)/2$$

Considering the optical path length with regard to each individual layer, then:

$$2n_1 d_1 = \lambda/2,$$

thus

$$d_1 = \lambda/4n_1 \qquad (4)$$

and

$$2n_2 d_2 = \lambda/2,$$

thus

$$d_2 = \lambda/4n_2 \qquad (5)$$

Accordingly, by satisfying the equation (4) or (5), the thickness of each layer can be determined. In the present embodiment:

$$n_1 = 0.91 + 6.8 \times 10^{-3}i$$

$$n_2 = 1.02 + 3.7 \times 10^{-3}i$$

$$\lambda = 12.4 \text{ nm} (124 \text{ Å})$$

Since the imaginary number portion is very small as compared with the real number portion, it may be considered as "zero". By substituting these values into equations (4) and (5), the thicknesses can be determined as follows:

$$d_1 \fallingdotseq 2.98 \text{ nm} (29.8 \text{ Å})$$

$$d_2 \fallingdotseq 3.39 \text{ nm} (33.9 \text{ Å})$$

In the particular example described hereinbefore, after the reflective base portion of the multilayered structure was obtained, a resist layer of PMMA was formed on the reflective base portion with a thickness 0.5 μm . Subsequently, by use of electron-beam patterning process, the resist layer was patterned with 1.75 μm line-and-space. Then, gold (linear expansion coefficient: 1.42×10^{-5}/deg and heat conductivity: 3.16 J/cm.s.deg) was deposited on the resist layer, by electron beam deposition and with a thickness of 0.1 μm (Figure 3B). As is well known in the art, gold is a material that can absorb soft X-rays. Subsequently, the PMMA material was removed, whereby a gold pattern A was obtained on the multilayered film (see Figure 3C).

Another example of the first embodiment will now be described. The mask of this example may be suitably used with a radiation having a wavelength of 12.4 nm (124 Å) and with an angle of incidence θ=0 (degree).

As in the foregoing example, a ground silicon single crystal plate 1 was used. As the material of the first type layers 2, 4, ..., tantalum nitride (TaN) having a refractive index N = 0.96 + 3.7 x 10^{-2}i was used. On the other hand, as the material of the second type layers 3, 5, ..., silicon (Si) having a refractive index N = 1.03 + 1.5 x 10^{-3}i was used. After a super high vacuum pressure not greater than 1 x 10^{-6} Pa was achieved, forty-one layers (twenty-one layers of TaN and twenty layers of Si) were formed

with respective thicknesses 2.03 nm (20.3Å) and 4.06 nm (40.6Å), by sputtering deposition while retaining an argon pressure 5 x 10^{-1} Pa. Additionally, upon the top layer, a layer of carbon (C) was formed with a thickness 1.0 nm (10Å) as a protection film B. In this example, the first type layers have a refractive index whose real number portion is smaller, while the second type layers have a refractive index whose real number portion is larger. The thickness of each of the first type layer and the second-type layer can be determined in accordance with equation (1) related to the Bragg diffraction, as described hereinbefore.

PMMA layer of a thickness 0.5 μm was formed on the thus obtained reflective base portion of multilayered structure, and the PMMA layer was patterned by electron-beam patterning process. On the resultant PMMA pattern, tantalum (Ta) (linear expansion coefficient: 6.3×10^{-6}/deg and heat conductivity: 0.575 J/cm.s.deg) which is a soft X-ray absorbing material was deposited by electron-beam deposition with a thickness 0.1 μm . Subsequently, the PMMA material was removed, such that a tantalum pattern was obtained on the multilayered film.

Description will now be made of a third example of the first embodiment. The mask of this example may be suitably used with a radiation having a wavelength of 12.4 nm (124 Å) and with an angle of incidence θ=0 (degree).

As in the first example, a ground silicon single crystal plate was used. As for the material of the first type layers 2, 4, ..., palladium (Pd) having a refractive index N = 0.90 + 2.4 x 10^{-2}i was used. As the material of the second type layers 3, 5, ..., silicon (Si) having a refractive index N = 1.03 + 1.5 x 10^{-3}i was used. In a super high vacuum pressure not greater than 1 x 10^{-6} Pa, forty-one layers (twenty-one layers of Pd and twenty layers of Si) were formed on the substrate by electron-beam deposition, with respective thicknesses 2.11 nm (21.1 Å) and 4.03 nm (40.3Å). Further, a layer of carbon (C) of a thickness 1.0 nm (10Å) was formed thereupon as a protection film. In this example, the first type layers have a refractive index whose real number portion is smaller and the second type layers have a refractive index whose real number portion is larger.

Subsequently, a PMMA layer of a thickness 0.5 μm was formed on the thus obtained reflective base portion of multilayered structure, and, then, the PMMA layer was patterned by electron-beam patterning process. On the thus formed PMMA pattern, silicon (Si) (linear expansion coefficient: 2.6×10^{-6}/deg and heat conductivity: 1.49J/cm.s.deg) which is a soft X-ray absorbing material was deposited by electron-beam deposition to a thickness of 0.1 um. Subsequently, the PMMA material was removed, with the result that a silicon pattern was obtained on the multilayered film.

While, in these examples, a silicon single crystal plate is used as the substrate, the material is not limited thereto. For example, a glass plate, a fused silica plate,

a silicon carbide plate or otherwise may be used, provided that its surface is made sufficiently smooth, by grinding, as compared with the wavelength of radiation to be used.

Figure 4 shows a reflection type mask according to a second embodiment of the present invention. Figure 5 is a schematic illustration for explaining a problem which can be solved by the present embodiment.

In a case where a printing light such as soft X-rays is projected upon the mask with a substantial angle of inclination, as shown in Figure 5, there occurs "half shade" (23 in Figure 5) on the surface of the reflective portion of the mask, due to the thickness of the mask pattern. The present embodiment can minimize such half shade.

In Figure 5, denoted at 21 are non-reflective elements patterned on a reflective base portion of a multilayered film structure. Denoted at 20 are reflecting portions, and denoted at 25 is a substrate.

It will be readily understood from Figure 5 that the half shade 23 can be reduced by reducing the thickness (height) of the non-reflective pattern 21. Actually, however, to do so might be very difficult since an ordinary X-ray absorbing material does not have a high X-ray absorbing efficiency so that a substantial thickness is required for the material to provide a sufficient X-ray absorbing function.

In the embodiment shown in Figure 4, the non-reflective pattern is provided by a multilayered film structure which is arranged so that, by the interference effect, the light reflected from the upper surface of a first layer (such as d_1) and the light reflected from the upper surface of a second layer (such as d_2) act upon one another to mutually weaken the intensity. The layer thickness is determined for this purpose. As a result, the non-reflective portion D can function as an anti-reflection film.

It has been confirmed that the non-reflective portion D of the multilayered structure can be reduced in thickness significantly while retaining high non-reflection efficiency, as compared with that of a non-reflective portion simply made of an X-ray absorbing material.

Referring back to Figure 4, the mask of the present embodiment has a reflective base portion 10 comprising a multilayered film showing reflectivity to soft X-rays or otherwise. The reflective portion 10 is formed on a non-reflective flat substrate 1 made of a material absorbing soft X-rays or otherwise. The non-reflective portion D comprises a multilayered film and is formed on the reflective portion 10, to thereby provide a predetermined pattern.

The reflective portion 10 is formed by layering two different materials having different optical constants to provide first type layers 2, 4, 6, ... and second type layers 3, 5, 7, ... in an alternate fashion.

The thicknesses d_1, d_2, d_3, d_4, ... of the two types of layers are not less than 1.0 nm (10 Å). Each type of layers may have the same thickness (i.e. $d_1=d_3=...$, and $d_2=d_4=...$). Alternatively, all the layers may have different

thicknesses.

However, in consideration of (i) reduction in amplitude of the soft X-rays or vacuum ultraviolet rays due to the absorption thereof by each layer and (ii) mutual intensification of reflected lights due to the overlap of the phases of the reflected lights, at the interfaces of the layers, it is desirable to determine the thickness so that highest reflection factor is obtainable by the reflective portion as a whole. Where the thickness of each layer is less than 1.0 nm (10Å), it is difficult to achieve high reflection factor at the reflective portion because of the dispersion effect of the two materials at the interface. This is undesirable. With the increase in the number of layers, the reflection factor can be improved. On the other hand, however, there will occur a difficulty in relation to the manufacture. Accordingly, the number of layers may preferably be not greater than two hundred.

The non-reflective portion D comprises alternately provided layers made of the different materials and constitutes an anti-reflection film to the reflective portion 10. The thicknesses $\tilde{a}_1, \tilde{a}_2, \tilde{a}_3, \tilde{a}_4$, ... of the layers forming the non-reflective portion D are not less than 1.0 nm (10Å). Alternating layers may have the same thickness (i.e. $\tilde{a}_1=\tilde{a}_3=...$, and $\tilde{a}_2=\tilde{a}_4=...$). Alternatively, all the layers may have different thicknesses.

It is desirable that a reflection type mask has an intensity ratio of 2:1, preferably 10:1, in respect to the intensities of the soft X-rays or otherwise reflected by the reflective portion 10 and the non-reflective portion D, respectively. For this reason, the anti-reflection film may preferably be formed by two or more layers, although the number intimately depends upon the wavelength range to be used. For the soft X-rays or otherwise of a wavelength near 10.0 nm (100Å), for example, the provision of three or more layers is preferable.

From equation (1) related to the Bragg diffraction theory, it is seen that the following condition should be satisfied in order that a layered film can function as an anti-reflection film:

$$2(n_1 d_1 + n_2 d_2)\cos\theta = \lambda(2m+1)/2$$

wherein m is an integral number.

From this, it is seen that each layer of the anti-reflection film has a thickness approximately of an order of $\lambda/4n$ wherein λ is the wavelength and n is the refractive index.

Description will now be made of a particular example of a mask according to the second embodiment. The mask of this example may be suitably used with the wavelength of 12.4 (124Å) and with the angle of incidence θ =10 degrees.

In this example, a silicon single crystal plate which has been ground to a surface roughness not greater than 1.0 nm (10Å) (rms) was used as the substrate 1 (Figure 6A). As the material of the first type layers 2, 4, 6, ..., molybdenum (Mo) having a refractive index N =

0.95 + 8.9 x 10^{-3}i, a linear expansion coefficient of 5.0 x 10^{-6} K^{-1} and heat conductivity of 139 w/mK, was used. On the other hand, as the material of the second type layers 3, 5, 7, ..., silicon (Si) having a refractive index N = 1.03 + 1.5 x 10^{-3}i, a linear expansion coefficient of 2.5 x 10^{-6} K^{-1} and a heat conductivity of 168 w/mK, was used. After a super high vacuum pressure not greater than 1x10^{-6} Pa was achieved, forty-one layers (twenty-one layers of Mo and twenty layers of Si) were formed on the substrates with a thickness 2.7 nm (27Å) (for each first type layer Mo) and a thickness 38.9 nm (38.9Å) (for each second type layer Si), by sputtering deposition while maintaining an argon pressure of 5x10^{-2} Pa. Thus, the reflective base portion 10 was formed. Subsequently, a carbon layer was formed on the reflective portion 10 as a protection film B. The thicknesses were determined in the same manner as in the examples described hereinbefore.

In this example, the selection of materials is made so that the first type layers (Mo) have a refractive index whose real number portion is smaller while the second type layers (Si) have a refractive index whose real number portion is larger.

Subsequently, as shown in Figure 6B, a layer of a resist material PMMA was formed on the reflective portion 10 with a thickness 0.5 micron. Then, by electron beam patterning, the PMMA layer was patterned with 1.75 µm line-and-space. As a result, a patterned resist layer of PMMA was obtained.

Upon the thus formed PMMA resist pattern, silicon (Si) and molybdenum (Mo) were alternately deposited by sputtering deposition to form thirteen alternate layers of Si and Mo having thicknesses 7.1, 3.7, 3.1, ..., 3.6, 3.2, 3.6 and 3.3 nm (71, 37, 31, ..., 36, 32, 36 and 33Å). The conditions of the sputtering deposition were the same as those at the time of manufacture of the reflective portion 10. The thicknesses are those that satisfy "λ/4n" described hereinbefore.

Subsequently, the resist material was removed, with the result that non-reflective elements 31 of multilayered film structure were formed on the reflective portion 10 (Figure 6C). The thickness of the non-reflective portion 31 as a whole was 48.0 nm (480 Å).

In order to confirm the anti-reflection effect of the non-reflective portion to the reflective portion, at time of the sputtering deposition during the manufacture of the reflection type mask (at the time of formation of the reflective portion and the non-reflective portion), reference samples were also placed in a deposition apparatus. At the time of formation of the reflective portion, three reference samples were set and, at the time of formation of the non-reflective portion, one of them was set again. This was done to allow measurement of the reflection factor of a reflective portion and the reflection factor of a reflective portion having a non-reflective portion formed thereon. By the measurement with a wavelength 13.0 nm (130 Å) and with an angle of incidence of 10 degrees, it was confirmed that the former has a reflec-

tion factor of 52 % and the latter has a reflection factor of 28 %.

In order to confirm the thickness which might be required if the non-reflective portion is formed simply by an absorptive material, examination has been made. For this examination, molybdenum (Mo) was deposited on the reflective portion of a reference sample to a thickness 300 nm (3000 Å) and the reflection factor was measured under the same conditions described hereinbefore. The reflector factor of 3.4 % was measured. Thus, it has been confirmed that an absorption layer of a large thickness is required if the non-reflective portion is formed only by an absorptive material.

Description will now be made of a second example of a mask according to the second embodiment of the present invention. The mask of this example may be used with a wavelength of 12.4 nm (124 Å).

In a similar manner as the example of Figures 6A-6C, a reflective portion 10 was formed on a substrate 1. Further, a pattern of a predetermined configuration was formed on the reflective portion by use of a resist material PMMA. Then, after a high vacuum not greater than 1x10^{-6} Pa was achieved, carbon (C) having a refractive index N = 0.97 + 5.2 x 10^{-3}i, a linear expansion coefficient 3.8x10^{-6} K^{-1} and a heat conductivity 130 w/mK and tungsten (W) having a refractive index N = 0.95 + 3.9 x 10^{-2}i, a linear expansion coefficient 5 x 10^{-6} K^{-1} and a heat conductivity 178 w/mK, were alternately deposited by sputtering deposition while maintaining an argon pressure of 5x10^{-2} Pa, such that a non-reflective portion comprising six layers having thicknesses 7.3, 10.8, 2.9, 3.8, 3.0 and 4.0 nm (73, 108, 29, 38, 30 and 40 Å) was formed. The thicknesses were determined in the same manner as the foregoing example. Subsequently, the resist material PMMA was removed, with the result that a mask having a reflective portion of multilayered film structure and a non-reflective portion formed on the reflective portion and having a multilayered film structure, was obtained. The thickness of the non-reflective portion as a whole was 31.8 nm (318 Å). Also in this example, reference samples were prepared so as to confirm the anti-reflection effect of the non-reflective portion. For the reflective portion, a reflection factor of 52% was measured with a wavelength 13.0 nm (130 Å) and an angle of incidence of 1.0 degree. For the non-reflective portion formed on the reflective portion, a reflection factor 3.2 % was measured. On the other hand, for an absorptive element provided by depositing tungsten on the surface of the reflective portion of the sample with a thickness 72.0 nm (720 Å a reflection factor of 4.7 % was measured. Thus, it was confirmed that, in order that an absorptive element made of an absorptive material provides substantially the same effect as of a non-reflective portion made of a multilayered film, the absorptive element must has a thickness twice or more greater than the thickness of the non-reflective portion of multilayered film structure.

In the examples of the second embodiment, the pro-

tection film provided on the upper surface of the reflective portion is preferably made by a carbon layer of a thickness not greater than than 10.0 nm (100Å). However, such a protection film may be omitted.

While, in the present embodiment, the multilayered structure of the reflective portion is formed by alternately layering two different materials, three or more materials may be used and layered in sequence.

Further, while a silicon single crystal plate is used in the present embodiment as a substrate, the material is not limited thereto. A glass plate, a fused silica plate, a silicon carbide plate or otherwise may be used, provided that its surface is made sufficiently smooth, by grinding, as compared with the wavelength to be used.

Figure 7 shows the structure of a reflection type mask according to a third embodiment of the present invention.

Briefly, in the present embodiment, a mask pattern is formed by selectively irradiating a reflective base portion of multilayered film structure with a particular radiation beam so as to change the physical and/or chemical characteristics of the reflective portion to thereby destroy the regularity of the multilayered structure in the portion irradiated by the radiation beam.

A particular example of a reflection type mask according to the present embodiment will be described. The mask of this example may be suitably used with a wavelength of 12.4 nm (124Å) and an angle of incidence $\theta=0$ (degree).

As a substrate 1, a ground quartz plate having a surface roughness not greater than 0.2 nm (2Å) (rms) was used. On the substrate 1, molybdenum (Mo) having a refractive index $N = 0.93 + 8.9 \times 10^{-3}i$, a linear expansion coefficient $5.0 \times 10^{-6} K^{-1}$ and a heat conductivity 139 w/mK and silicon (Si) having a refractive index $N = 1.03 + 1.5 \times 10^{-3}i$ were deposited alternately by ion-beam sputtering deposition, in a high vacuum pressure not greater than 7×10^{-5} Pa (5×10^{-7} Torr) while maintaining an argon pressure of 3×10^{-2} Pa (2×10^{-4} Torr) and by use of a rock crystal oscillator type film thickness monitor. Forty-one layers (twenty-one layers of Mo and twenty layers of Si) were formed in an alternately layered fashion to provide first type layers 2, 4, 6, ... made of Mo and second type layers 3, 5, 7, ... made of Si. The thickness of each of the first type layers (Mo) was 2.7 nm (27Å) and the thickness of each of the second type layers (Si) was 3.6 nm (36Å). The thickness was determined similarly as in the examples described hereinbefore.

In this example, the selection of materials for the first and second layers has been made so that the first type layers (Mo) have a refractive index whose real number portion is smaller while the second type layers (Si) have a refractive index whose real number portion is larger.

Next, by using a converging ion-beam scanning apparatus, the thus formed reflective portion comprising a multilayered film was irradiated with a focused silicon ion beam having a focused beam diameter of 0.1 μm

under an acceleration voltage 200 Kev. As a result, the regularity of the layered structure of the part of the reflective portion 10 irradiated with the ion beam was destroyed so that the irradiated part of the reflective portion 10 lost the function of a "reflecting surface". In the manner described, a plurality of non-reflective portions 22 were formed in the reflective portion 10 and a pattern of 0.8 μm line-and-space was obtained. The beam current was 100 PA.

Measurements were made with regard to the reflection factors at the positions corresponding to the reflective portion and the non-reflective portion of the obtained reflection type mask, and it was confirmed that the former had a reflection factor of 48 % and the latter had a reflection factor of 0.8 %. Thus, the contrast was 60:1.

Another example of a mask according to the fourth embodiment of the present invention will now be described. The mask of this example may be suitably used with a wavelength of 12.4 nm (124Å) and an angle of incidence $\theta=0$ (degree).

As in the foregoing example, a ground quartz plate was used as a substrate 1 and, on that substrate, first type layers 2, 4, ... made of ruthenium (Ru) having a refractive index $N = 0.91 + 6.8 \times 10^{-3}i$ and second type layers 3, 5, ... made of silicon (Si) having a refractive index $N = 1.03 + 1.5 \times 10^{-3}i$ were formed in an alternate fashion, in a super high vacuum pressure not greater than 1×10^{-7} Pa (1×10^{-9} Torr) by means of electron-beam deposition and by use of a rock-crystal oscillator type film thickness monitor. Forty-one layers (twenty-one layers of Ru and twenty layers of Si) were formed with a thickness 2.7 nm (27Å) (for each Ru layer) and a thickness 3.6 nm (36 Å) (for each Si layer). The thickness was determined in the same manner as in the foregoing example.

Next, the thus obtained reflective portion of multilayered film structure was selectively irradiated with a focused argon laser beam with an output power of 5 W. As a result, the regularity of the layered structure of the part of the reflective portion irradiated with the laser beam was destroyed so that the irradiated part lost the function as a "reflecting surface". In the manner described, non-reflective portions 22 formed in the reflective portion and a pattern of 1 μm line-and-space was obtained.

The means for destroying the regularity of the layered structure is not limited to the converging ion-beam scanning apparatus or the use of a laser beam.

For example, an electron beam may be used. It is a further alternative that a resist pattern is first formed on a multilayered film and a glass plasma is used to destroy the regularity of the layered structure, the resist material being thereafter removed.

It should be noted that a reflection type mask will be used, in many cases, with an intense X-ray source such as, for example, a light source means using a synchrotron emission light source. Thus, it will be necessary to consider the problem of a temperature increase due

to the absorption of a radiation energy by the mask. Particularly, the thermal expansion due to the temperature increase will cause shift of the position of a pattern on the mask surface or distortion of the mask pattern. This is a very serious problem in the reproduction of patterns having a submicrometre linewidth.

In consideration of this, it will be desirable to suppress any temperature increase in the reflection type mask due to the absorption of soft X-rays or otherwise by the mask.

In the reflection type mask according to any one of the above-described embodiments, a bulk material may be used as the substrate. Thus, the mask itself can be cooled by water or otherwise. Therefore, it is possible to diminish, remarkably, the adverse effect of the temperature increase in the mask. Further, by using a material (examples of which will be described later) having a high heat conductivity as for the substrate and the multilayered film, the heat can be radiated efficiently with an advantageous effect of prevention of the temperature increase.

Moreover, in the embodiments described hereinbefore, a material (examples of which will be described later) having a small linear expansion coefficient may be used as the substrate and the multilayered film. This is effective to suppress the occurrence of distortion due to the temperature increase.

As for the material of the substrate which may be used preferably, there are silicon carbide, aluminum nitride, silicon nitride of ceramics series, for example. Particularly, the silicon carbide is preferable because it has a very large heat conductivity (of an order of 100 w/mK). As for the material usable in the multilayered film as one type layer, there are transition metal such as tungsten, tantalum, molybdenum, rhodium, ruthenium or otherwise, carbide, nitride, silicide, boride, oxide or otherwise of any one of the aforementioned transition metals. As for the material which may be used as the other type layer, there are silicon, beryllium, carbon, boron, composite of these materials (e.g. silicon carbide, boron carbide), oxide, nitride or otherwise of these materials such as silicon oxide, silicon nitride and so on.

Particularly, the silicon carbide has a linear expansion coefficient of not greater than 4.5×10^{-6} K^{-1} and the tungsten has a linear expansion coeffcient of not greater than 4.5×10^{-6} K^{-1}, so that they are preferble. Further, molybdenum usable as the material of the reflective portion has a linear expansion coefficient of not greater than 4.8×10^{-6} K^{-1}, and therefore molybdenum is a preferable material.

In the embodiments described hereinbefore, it is preferable to use a material having a linear expansion coefficient not greater than 1×10^{-5}/K and a heat conductivity not less than 20 w/mK, as for the material of the substrate, the material of the reflective portion and the material of the non-reflective portion.

The manufacture of the multilayered film is not limited to use of the ion-beam sputtering method or the electron-beam deposition method using a super high vacuum. Other thin film manufacturing techniques such as double-electrode sputtering method, organic metal chemical vapour deposition method (called "MOCVD method"), etc., may be adopted.

In the embodiments described hereinbefore, if it is desired to correct any "curvature of field" which might be caused in the imaging optical system such as illustrated in Figure 1, the mask may be formed so that the substrate thereof has a curved surface such as, for example, a spherical surface, an aspherical surface, an asymmetrically curved surface, etc.

While the invention has been described with reference to the structures disclosed herein, it is not confined to the details set forth and is intended to cover such modifications or changes as may come within the scope of the following claims.

Claims

1. A reflection type mask (Mo) usable in an exposure apparatus having a projection optical system with a plurality of mirrors (M1,M2,M3) provided between the mask and a workpiece (W) for transferring a pattern of the mask onto the workpiece with soft X-ray or vacuum ultraviolet radiation, characterized in that:

   said mask (Mo) has a reflective surface (10; 10;24) provided by a multilayered film (2-5;2-5;2-5), and a non-reflective portion (A;D;21;22) provided in or upon said reflective surface to define the pattern, and wherein said non-reflective portion (A;D;21;22) is effective to attenuate the soft X-ray or vacuum ultraviolet radiation.

2. A mask according to Claim 1, wherein said non-reflective portion (A;D;21) comprises an absorbing material provided upon said multilayered film (2-5; 2-5;24).

3. A mask according to Claim 1, wherein said non-reflective portion (22) is a disordered portion (22) of said multilayered film (2-5).

4. A reflection type mask according to Claim 1, wherein said absorbing material of said non-reflective portion (A;D;21;22) has a linear expansion coefficient not greater than 5×10^{-5} deg^{-1} and a heat conductivity not less than 0.1 J/cm.s.deg.

5. A reflection type mask according to Claim 1, wherein said multilayered film (2-5) is formed of alternate layers (2,3,4,5) of respective different materials having different optical constants.

6. A reflection type mask according to Claim 5, wherein said multilayered film has first layers (2,4,...) hav-

ing a refractive index whose real number portion is smaller and second alternate layers (3,5,...) having a refractive index whose real number portion is larger, which first and second layers (2-5) are respectively further from and nearer to the reflection type mask surface.

7. An exposure method for transferring a pattern of a reflection type mask onto a workpiece with soft X-ray or vacuum ultraviolet ray radiation, said method comprising the steps of:

   providing a reflection type mask (Mo) as claimed in any preceding Claim 1 to 6; and irradiating the mask (Mo) with said radiation, and exposing the workpiece (W) to radiation reflected by the mask (Mo) through a projection optical system having a plurality of mirrors (M1,M2,M3), whereby the pattern of the mask (Mo) is transferred to the workpiece (W).

8. A method according to Claim 7, wherein the pattern of the mask (Mo) projected onto the workpiece (W) is of a reduced scale.

9. An exposure apparatus for transferring a pattern of a reflection type mask onto a workpiece with soft X-ray or vacuum ultraviolet ray radiation, said apparatus comprising:

   holding means for holding a reflection type mask (Mo);
   a reflection type mask (Mo) held by said holding means, which mask (Mo) is as claimed in any preceding Claim 1 to 6; and
   optical means for irradiating the mask (Mo) with said radiation, and exposing the workpiece (W) to the radiation reflected by the mask (Mo), said optical means comprising a projection optical system having a plurality of mirrors (M1,M2,M3) for projecting the pattern of the mask onto the workpiece, whereby the pattern of the mask (Mo) is transferred to the workpiece (W).

10. An apparatus according to Claim 9, further comprising an optical system for projecting the pattern of the mask (Mo) onto the workpiece at a reduced scale.

Patentansprüche

1. Reflexionsmaske (Mo), die in einer Belichtungsapparatur mit einem optischen Projektionssystem verwendet werden kann, das eine Vielzahl an Spiegeln (M1,M2,M3) aufweist, die zwischen der Maske und einem Werkstück (W) angeordnet sind, um mittels weicher Röntgenstrahlung oder Vakuum-UV-Strahlung ein Maskenmuster auf das Werkstück zu übertragen, **dadurch gekennzeichnet, daß** die Maske eine reflektierende Oberfläche (10;10; 24), die von einem mehrschichtigen Film (2-5;2-5; 2-5) bereitgestellt wird, und einen nichtreflektierenden Bereich (A;D;21;22) aufweist, der in oder auf der reflektierenden Oberfläche bereitgestellt wird, um das Muster festzulegen, wobei der nicht-reflektierende Bereich (A;D;21;22) eine Schwächung der weichen Röntgenstrahlung oder der Vakuum-UV-Strahlung bewirkt.

2. Maske nach Anspruch 1,
   dadurch gekennzeichnet, daß
   der nicht-reflektierende Bereich (A;D;21) ein absorbierendes Material umfaßt, das auf dem mehrschichtigen Film (2-5;2-5;24) aufgebracht ist.

3. Maske nach Anspruch 1,
   dadurch gekennzeichnet, daß
   der nicht-reflektierende Bereich (22) ein ungeordneter Bereich (22) des mehrschichtigen Films (2-5) ist.

4. Reflexionsmaske nach Anspruch 1,
   dadurch gekennzeichnet, daß
   das absorbierende Material des nicht-reflektierenden Bereichs (A;D;21;22) einen linearen Ausdehnungskoeffizienten, der nicht größer als 5×10^{-5} deg^{-1} ist, und eine Wärmeleitfähigkeit von nicht kleiner als 0,1 J/cm.s.deg aufweist.

5. Reflexionsmaske nach Anspruch 1,
   dadurch gekennzeichnet, daß
   der mehrschichtige Film (2-5) aus alternierenden Schichten (2,3,4,5) aus jeweils unterschiedlichen Materialien mit unterschiedlichen optischen Konstanten gebildet ist.

6. Reflexionsmaske nach Anspruch 5,
   dadurch gekennzeichnet, daß
   der mehrschichtige Film erste Schichten (2,4,...) mit einem Brechungsindex, dessen Realteil kleiner ist, und zweite, alternierende Schichten (3,5,...) mit einem Brechungsindex, dessen Realteil größer ist, aufweist, wobei sich die ersten und zweiten Schichten (2-5) weiter weg von beziehungsweise näher an der Oberfläche der Reflexionsmaske befinden.

7. Belichtungsverfahren zum Übertragen eines Musters einer Reflexionsmaske auf ein Werkstück mittels weicher Röntgenstrahlung oder Vakuum-UV-Strahlung, wobei das Verfahren die nachstehenden Schritte umfaßt:

   Bereitstellung einer Reflexionsmaske (Mo) nach einem der vorstehenden Ansprüche 1 bis

6; und

Bestrahlen der Maske (Mo) mit der Strahlung und Aussetzen des Werkstücks (W) der von der Maske (Mo) reflektierten Strahlung mittels eines optisches Projektionssystem, das eine Vielzahl an Spiegeln (M1, M2, M3) aufweist, wodurch das Muster der Maske (Mo) auf das Werkstück (W) übertragen wird.

8. Verfahren nach Anspruch 7, in dem das Muster der Maske (Mo), das auf das Werkstück projeziert wird, einen verkleinerten Maßstab aufweist.

9. Belichtungsgerät zum Übertragen eines Musters einer Reflexionsmaske mittels weicher Röntgenstrahlung oder Vakuum-UV-Strahlung auf ein Werkstück, wobei das Gerät die nachstehenden Bestandteile umfaßt:

eine Halteeinrichtung zum Halten der Reflexionsmaske (Mo);

eine Reflexionsmaske (Mo), die von der Halteeinrichtung gehalten wird, wobei es sich um eine Maske (Mo) nach einem der vorstehenden Ansprüche 1 bis 6 handelt; und

eine optische Einrichtung zum Bestrahlen der Maske (Mo) mit der Strahlung und zum Belichten des Werkstücks (W) mit der von der Maske (Mo) reflektierten Strahlung, wobei die optische Einrichtung ein optisches Projektionssystem mit einer Vielzahl an Spiegeln (M1,M2,M3) zum Projezieren des Musters der Maske auf das Werkstück umfaßt, wodurch das Muster der Maske (Mo) auf das Werkstück (W) übertragen wird.

10. Gerät nach Anspruch 9, das ferner ein optisches System zum Projezieren des Musters der Maske (Mo) in verkleinertem Maßstab auf das Werkstück umfaßt.

Revendications

1. Masque (Mo) du type à réflexion, utilisable dans un appareil d'exposition comportant un système optique de projection avec plusieurs miroirs (M1, M2, M3) placés entre le masque et une pièce d'oeuvre (W) destinés à transférer un motif du masque sur la pièce d'oeuvre à l'aide d'un rayonnement de rayons X mous ou d'ultraviolet lointain, caractérisé en ce que :

ledit masque (Mo) possède une surface réfléchissante (10 ; 10 ; 24) constituée par un film multicouche (2 à 5 ; 2 à 5 ; 2 à 5), et une partie non

réfléchissante (A ; D ; 21 ; 22) prévue dans ou sur ladite surface réfléchissante pour définir le motif ; et dans lequel ladite partie non réfléchissante (A ; D ; 21 ; 22) sert à atténuer le rayonnement de rayons X mous ou d'ultraviolet lointain.

2. Masque selon la revendication 1, dans lequel ladite partie non réfléchissante (A ; D ; 21) comprend une matière absorbante disposée sur ledit film multicouche (2 à 5 ; 2 à 5 ; 24).

3. Masque selon la revendication 1, dans lequel ladite partie non réfléchissante (22) est une partie (22) dudit film multicouche (2 à 5) dont l'ordre a été modifié.

4. Masque du type à réflexion selon la revendication 1, dans lequel ladite matière absorbante de ladite partie non réfléchissante (A ; D ; 21 ; 22) a un coefficient de dilatation linéaire qui n'est pas plus grand que 5×10^{-5} deg^{-1} et une conductivité thermique qui n'est pas plus petite que 0,1 J/cm.s.deg.

5. Masque du type à réflexion selon la revendication 1, dans lequel ledit film multicouche (2 à 5) est formé de couches (2, 3, 4, 5) alternées de matières respectives différentes ayant des constantes optiques différentes.

6. Masque du type à réflexion selon la revendication 5, dans lequel ledit film multicouche comporte des premières couches (2, 4, ...) ayant un indice de réfraction dont la partie nombre réel est plus petite et des secondes couches alternées (3, 5, ...) ayant un indice de réfraction dont la partie nombre réel est plus grande, lesquelles premières et secondes couches (2 à 5) sont respectivement plus loin et plus près de la surface de masque du type à réflexion.

7. Procédé d'exposition destiné à transférer un motif d'un masque du type à réflexion sur une pièce d'oeuvre à l'aide d'un rayonnement de rayons X mous ou d'ultraviolet lointain, ledit procédé comprenant les étapes :

de création d'un masque (Mo) du type à réflexion tel que revendiqué dans l'une quelconque des revendications 1 à 6 précédentes ; et de projection dudit rayonnement sur le masque (Mo), et d'exposition de la pièce d'oeuvre (W) au rayonnement réfléchi par le masque (Mo), à l'aide d'un système optique de projection comportant plusieurs miroirs (M1, M2, M3), en transférant ainsi le motif du masque (Mo) sur la pièce d'oeuvre (W).

8. Procédé selon la revendication 7, dans lequel le motif du masque (Mo) projeté sur la pièce d'oeuvre (W) est à échelle réduite.

9. Appareil d'exposition destiné à transférer un motif d'un masque du type à réflexion sur une pièce d'oeuvre à l'aide d'un rayonnement de rayons X mous ou d'ultraviolet lointain, ledit appareil comprenant :

    un moyen de maintien destiné à maintenir un masque (Mo) du type à réflexion ;
un masque (Mo) du type à réflexion maintenu par ledit moyen de maintien, lequel masque (Mo) est tel que revendiqué dans l'une quelconque des revendications 1 à 6 précédentes ; et un moyen optique destiné à projeter ledit rayonnement sur le masque (Mo), et à exposer la pièce d'oeuvre (W) au rayonnement réfléchi par le masque (Mo), ledit moyen optique comprenant un système optique de projection comportant plusieurs miroirs (M1, M2, M3) destinés à projeter le motif du masque sur la pièce d'oeuvre, en transférant ainsi le motif du masque (Mo) sur la pièce d'oeuvre (W).

10. Appareil selon la revendication 9, comprenant en outre un système optique destiné à projeter le motif du masque (Mo) sur la pièce d'oeuvre à une échelle réduite.

FROM DIVERGENT
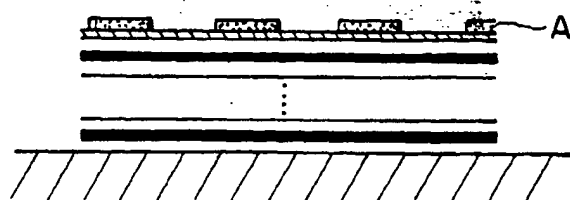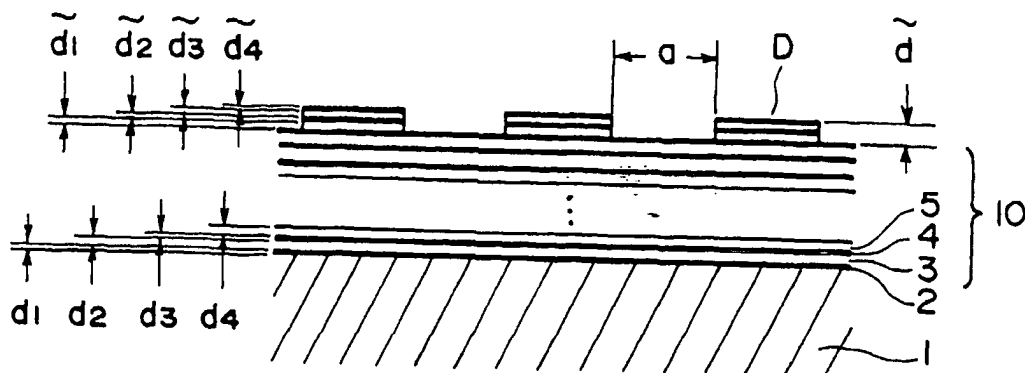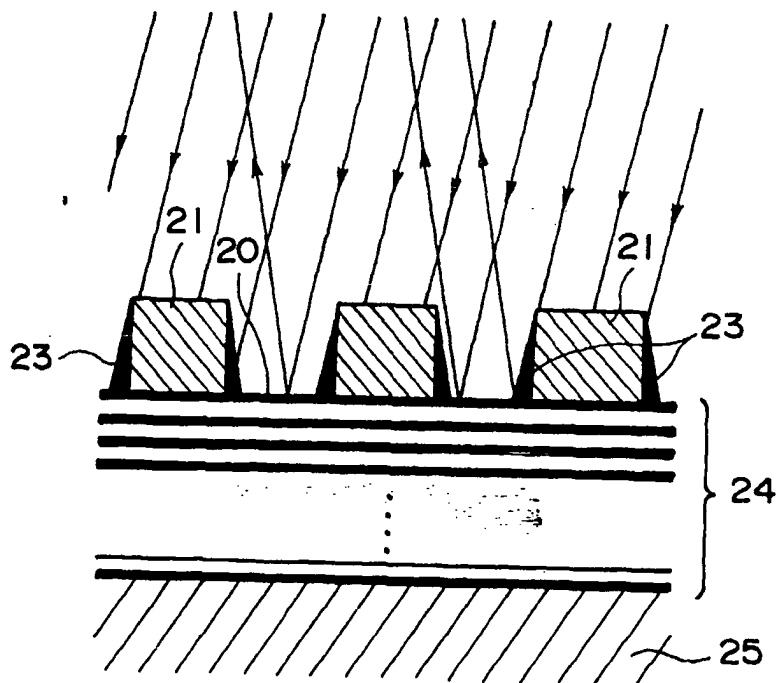X-RAY SOURCE

M1

M2

M3
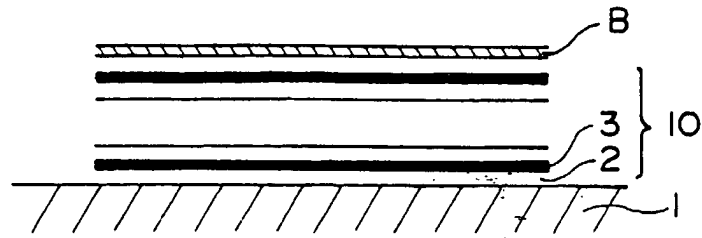
W

Mo

FIG. I
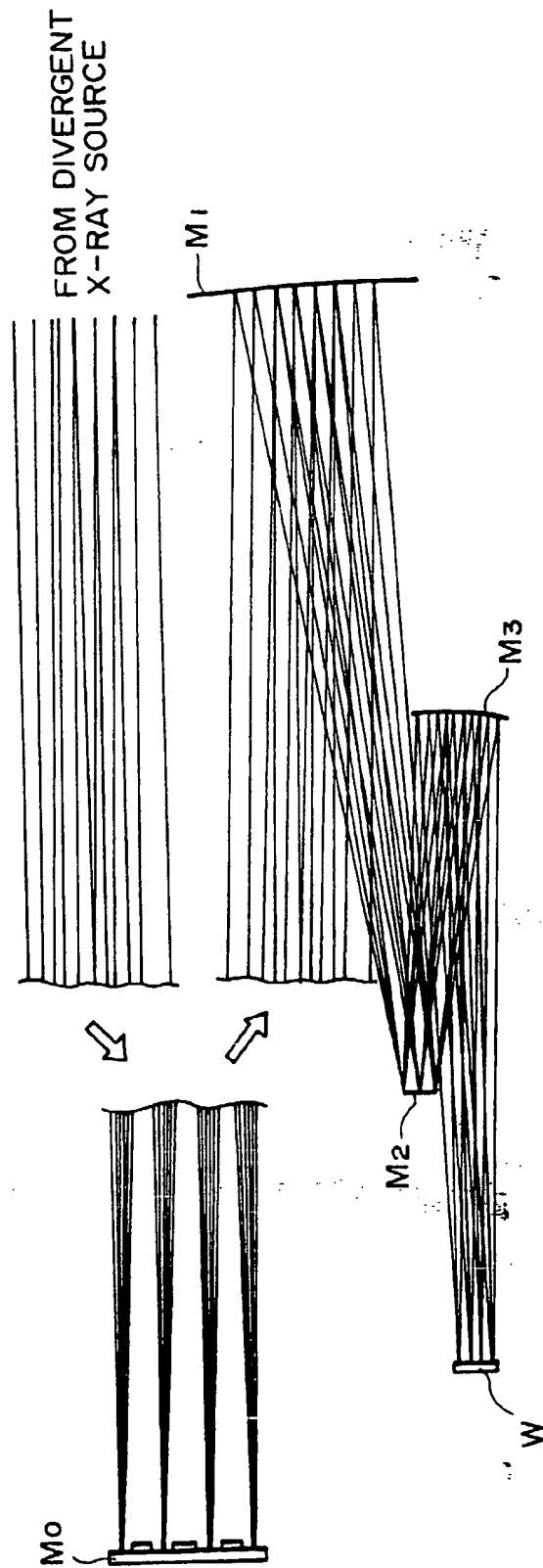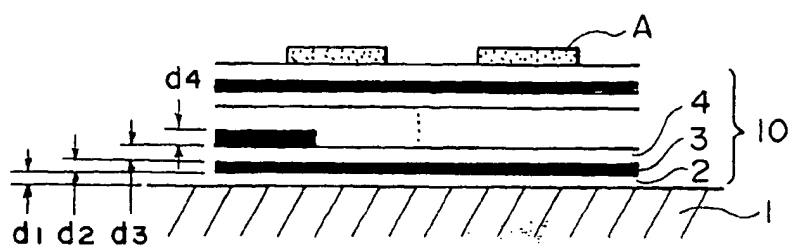
F I G. 2
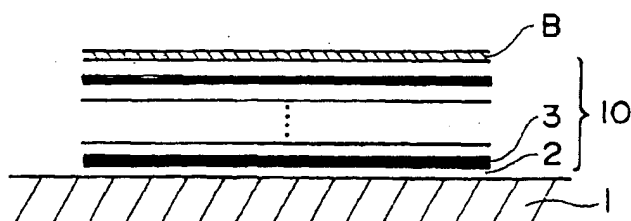
F I G. 3A
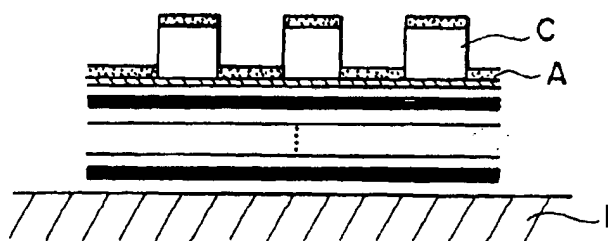
F I G. 3B

F I G. 3C

FIG. 4

FIG. 5

FIG. 6A

FIG. 6B

FIG. 6C

FIG. 7